(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 21 April 2005 (21.04.2005)

PCT

(10) International Publication Number WO 2005/034791 A1

(51) International Patent Classification7: C23C 16/32

A61C 3/02,

(21) International Application Number:

PCT/US2004/033534

(22) International Filing Date: 8 October 2004 (08.10.2004)

(25) Filing Language:

(26) Publication Language:

English

(30) Priority Data: 60/509,966

9 October 2003 (09.10.2003)

(71) Applicant and

(72) Inventor: SHAYGAN, Farzad [US/US]; 4040 Barranca Parkway, Suite 140, Irvine, California 92604 (US).

(74) Agent: ALTMAN, Daniel, E.?; KNOBBE, MARTENS, OLSON & BEAR, LLP, 2040 Main Street, Fourteenth Floor, Irvine, CA 92614 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

of inventorship (Rule 4.17(iv)) for US only

Published:

with international search report

before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A DRILL BIT WITH A MOISSANITE (SILICON CARBIDE) CUTTING ELEMENT

(57) Abstract: A cutting element for a rotary-type drill bit is disclosed comprising moissanite (silicon carbide) crystals impregnated within and/or coated on the surface of the cutting elements.



PCT/US2004/033534

A DRILL BIT WITH A MOISSANITE (SILICON CARBIDE) CUTTING ELEMENT

5

Related Applications

This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Application No. 60/509,966, filed on October 9, 2003, the entirety of which is hereby incorporated by reference.

Background of the Invention

10 Field of the Invention

Embodiments of the present invention relate to cutting elements for use in drill bits and dental burs. In particular, preferred embodiments of the present invention relate to a cutting element for use in drill bits and dental burs which include moissanite (silicon carbide) as an abrasive material.

15

20

25

30

Description of the Related Art

Rotary drill bits with no moving elements on them are typically referred to as "drag" bits. Drag bits are often used to drill very hard or abrasive formations, or where high bit rotation speeds are required.

Drag bits are typically made from a solid body of matrix material formed by a powder metallurgy process. The process of manufacturing such bits is known in the art. During manufacture, the bits are fitted with different types of cutting elements that are designed to penetrate the formation during drilling operations. One example of such a bit includes a plurality of polycrystalline diamond compact ("PDC") cutting elements arranged on the bit body to drill a hole. Another example of such bits uses much smaller cutting elements. The small cutting elements may include natural or synthetic diamonds that are embedded on the surface of the matrix body of the drill bit. Bits with surface set diamond cutting elements are especially well suited for hard formations which would quickly wear down or break off PDC cutters.

However, surface set cutting elements also present a disadvantage because, once the cutting elements are worn or sheared from the matrix, the bit has to be replaced because of decreased performance, including decreased rate of penetration.



5

10

15

20

25

30

PCT/US2004/033534

An improvement over surface set cutting elements is provided by diamond impregnated drill bits. Diamond impregnated bits are also typically manufactured through a powder metallurgy process. During the powder metallurgy process, abrasive particles are arranged within a mold to infiltrate the base matrix material. Upon cooling, the bit body includes the matrix material and the abrasive particles suspended both near and on the surface of the drill bit. The abrasive particles typically include small particles of natural or synthetic diamond. Synthetic diamond used in diamond impregnated drill bits is typically in the form of single crystals. However, thermally stable polycrystalline diamond particles may also be used.

The basic techniques for constructing polycrystalline diamond enhanced cutting elements are generally well known. They can be summarized as follows: a carbide substrate is formed having a desired surface configuration; the substrate is placed in a mold with a superhard material, such as diamond powder and/or a mixture of diamond with other material that forms transition layers, and subjected to high temperature and pressure, resulting in the formation of a diamond layer bonded to the substrate surface.

Although cutting elements having this configuration have significantly expanded the scope of formations for which drilling with diamond bits is economically viable, existing cutting elements are still prone to failure. For example, failure typically takes one of three common forms, namely (1) spalling/chipping, (2) delamination, and (3) wear. External loads due to contact tend to cause failures such as fracture, spalling, and chipping of the diamond layer. Internal stresses for example, thermal residual stresses resulting from manufacturing process, tend to cause delamination of the diamond layer, by cracks initiating in the diamond layer surface and propagating along the interface. Excessively high contact stress and high temperature are known to cause severe wear to the diamond layer of cutting elements in percussion bits. Wear is not a typical failure mode in roller cone drill bits that utilize conventional diamond coated cutting elements. Instead, fatigue and impact of the diamond coating typically result in spalling or delamination, depending upon the thermal-mechanical properties of the diamond or diamond-like coating

Inherent in conventional efforts to make a sharp and durable dental instrument is that these materials tend to be brittle, and crack and break. Breakage during a dental procedure represents danger to the patient. A piece of the instrument may come loose and not be readily retrievable, or may jam in a tooth crevice, requiring sacrificing some of the

5

10

15

20

25

30

PCT/US2004/033534

tooth. These tendencies may be countered not only by maintaining sharpness longer, but also by providing toughness as well.

Not surprisingly, there have been many attempts in the prior art to improve the durability of dental instruments. U.S. Pat. No. 4,190,958, issued Mar. 4, 1980 to Martin et al., discloses an endodontic drill file having a drilling surface coated with diamond particles. U.S. Pat. No. 4,466,795, issued Aug. 21, 1984, to Plischka, discloses a helocoidally grooved dental bur having a working surface covered with diamond particles. U.S. Pat. No. 4,681,541, issued Jul. 21, 1987 to Snaper, discloses a dental bur having a metal nitride or carbide layer applied over diamond particles. U.S. Pat. No. 4,731,019, issued Mar. 15, 1988 to Martin, discloses a scaler dental instrument that is coated with diamond particles. U.S. Pat. No. 4,895,146, issued Jan. 23, 1990 to Draenert, discloses a surgical bone grinding instrument having a coating of diamond particles in size of about 30 to about 250 microns.

Hence, there remains a need for an improved drill bit, particularly a dental drill bit, wherein the cutting elements comprise superhard crystalline abrasive materials, that provide increased resistance to fatigue, impact and wear compared to conventional diamond cutting elements, without increasing the risk of spalling or delamination.

Summary of the Invention

One preferred embodiment of the present invention comprises a rotary drill bit comprising a cutting element comprising moissanite (silicon carbide). In a preferred variation, the drill bit includes a cutting element comprising a continuous phase material impregnated and/or surface coated with moissanite (silicon carbide) crystals. Preferably, the continuous phase material includes a hard, erosion- and wear-resistant material, such as metal carbide, a refractory metal alloy, a ceramic, copper, a copper-based alloy, nickel, a nickel-based alloy, cobalt, a cobalt-based alloy, iron, or an iron-based alloy. In some embodiments, the impregnated and/or coated segment of the bit may include more than one type of crystalline abrasive material in addition to moissanite (silicon carbide), as well as one or more different sizes and structural configurations. The impregnated and/or coated segment may include a particulate mixture of moissanite (silicon carbide), diamond, cubic zirconium, carbonitride, amorphous carbon, and hydrogenated amorphous carbon or any other crystalline material having a hardness of greater than about 900 (H_v).

10

15

20

25

30

WO 2005/034791 PCT/US2004/033534

The moissanite (silicon carbide) preferably has a particle size ranging from about 8 to about 150 μm^3 . More preferably, the moissanite (silicon carbide) particle size ranges from about 25 to about 50 μm^3 . For example, various ranges of diamond particle sizes may be utilized in the manufacture to enhance wear properties as shown in U.S. Patent Nos. 4,861,350, 5,468,268, and 5,505,748, which are herein incorporated by reference in their entirety.

In another preferred embodiment of the present invention, a method is disclosed for preparing a moissanite (silicon carbide) impregnated cutting element. The impregnated cutting element is prepared by assembling layers of metal matrix material that contain interspersed moissanite. Each layer is formed by distributing the moissanite into a layer of bonding metal matrix. Each layer, which is assembled to form a superabrasive impregnated cutting element, can be of the same distribution pattern and concentration, or the distribution pattern and/or concentration may vary from layer to layer. These layers are then assembled to form the desired three-dimensional body. Subsequently the moissanite tool is consolidated by sintering or infiltration.

Detailed Description of the Preferred Embodiment

Preferred embodiments of the moissanite cutting element may be incorporated into drill bits used in dentistry, and other drilling applications known to those skilled in the art.

Moissanite is a crystalline material first discovered on a meteor. It is composed of silicon carbide. Accordingly, the silicon carbide material may be referred to herein as either silicon carbide or moissanite. The terms are used interchangeably herein and are so used by those of skill in the art. Moissanite has a very high hardness and a high refractive index. Furthermore, moissanite (silicon carbide) is a very tough material and an extremely stable material that can be heated to more than 2000 degrees F., in air, without suffering damage.

Silicon carbide is a complex material system that forms more than 150 different polytypes, each having different physical and electronic properties. The different polytypes can be classified in three basic forms: cubic, rhombohedral and hexagonal. Both the rhombohedral and hexagonal forms can occur in a number of different atomic arrangements that vary according to atomic stacking sequence.

Silicon carbide is commercially available and known in the trade as moissanite. Methods for making silicon carbide crystals are disclosed in 5,723,391, which is herein incorporated by reference in its entirety. Crystal is grown by an appropriate sublimation or

5

10

30

35

PCT/US2004/033534

deposition or other growth technique used to grow large (bulk) silicon carbide single crystals, with the preferred method being sublimation growth on a seed crystal. According to this preferred technique, crystal is grown by introducing a polished monocrystalline seed crystal of silicon carbide of a desired polytype into the furnace of a sublimation system along with silicon and carbon containing source gas or powder (source material). The source material is heated to a temperature that causes the source material to create a vapor flux that deposits vaporized Si, Si₂C, and SiC₂ to the growth surface of the seed crystal. The reproducible growth of a single selected polytype on the seed crystal is achieved by maintaining a constant flux of Si, Si₂C and SiC₂, and by controlling the thermal gradient between the source material and the seed crystal.

Silicon carbide crystals exhibit high hardness. The hardness and density of silicon carbide are compared with other stones below:

15	Hardness Density (Mohs) (SG)
	Emerald 7.5 2.5
	Corundum (sap & ruby)
••	9 3.9
20	Diamond 10 3.5
	Silicon Carbide (6H)
	9 3.2
	Silicon Carbide (4H)
	9 3.2
25	Cubic Zirconia 7.5 4.7

As illustrated by the table above, silicon carbide, when produced in certain atomic arrangements with the controlled introduction of specific dopant atoms, is an excellent gemstone material that has physical characteristics comparing favorably with, or exceeding, those of corundum and emerald. In its undoped hexagonal and rhombohedral forms, silicon carbide is the best known candidate to replicate the characteristics of diamond.

Moissanite coated cutting elements may be prepared by chemical vapor deposition (CVD), as described for preparation of polycrystalline diamond coatings on drills. See for example, U.S. Pat. No. 5,009,705A to Yoshimura et al., which discloses a microdrill bit with a CVD polycrystalline diamond coating; U.S. Pat. Nos. 5,022,801 and 5,096,736 to Anthony et al., which teach high temperature CVD diamond coatings on slotted twist drills; U.S. Pat. No. 5,256,206 to Anthony et al., which discloses a high temperature CVD reactor

15

20

25

30

WO 2005/034791 PCT/US2004/033534

suitable for coating drills; JP 01257196 A2 to Ito et al., which teaches a method for uniform coating of a drill with CVD diamond by precession motion of the drill during deposition; EP-470447A1 to Anthony et al., which discloses a heated tubular reactor for CVD diamond deposition on drill bits and similar tools; and EP-528592A1 to Iacovangelo, which describes a masking technique to produce selected area deposition of CVD diamond onto a twist drill. The disclosures of all of the above-cited patents are incorporated herein in their entirety by reference thereto.

As an alternative or variation to CVD methods for coating the cutting element with moissanite and optionally with other crystalline materials, methods for preparing diamondlike carbon (DLC) may also be employed in accordance with some embodiments of the present invention. For example, JP0248106 to Katsumata discloses a method for manufacturing a DLC coating on drills; DD-215922A1 to Bollinger et al. teaches a method for uniform coating deposition on a twist drill, using an independent direct current (DC) electrical field near the substrate, which is optionally modulated with an alternating current (AC) electrical field to direct the coating ion flow from the source to the cathode substrate; DD-215923A1 to Bollinger et al. discloses an apparatus for ion coating a spiral drill containing a positively charged electrode shape, preferably a wire, to direct the ion flux to the drill surface, using a positive shielding electrode between the substrate holder and the electrode shape surrounding the drill, e.g. a helical-shaped anode surrounding the drill; GB 2122224A1 to Goode et al. discloses an ion beam method for applying a hard carbon coating onto tungsten carbide drills; and JP 611464112A to Tobioka et al. teaches deposition of a sputtered Ti adhesion layer, followed by a plasma-deposited carbon coating on tungsten carbide drills. The disclosures of all of the above-cited patents are incorporated herein in their entirety by reference thereto.

According to one preferred method of applying crystals to the drill bit, which is disclosed in detail in 5,653,812, and is herein incorporated by reference in its entirety, the surfaces of the substrates to be coated are first chemically de-greased to remove contaminants. In the second step, the substrates are inserted into the coating fixture of the present invention, then the loaded fixture is placed into a plasma deposition vacuum chamber and the appropriate electrical connections are made as described in the discussion of the apparatus of this invention. In the third step, the air in the chamber is evacuated. In the fourth step, a non-depositing gas, such as Ar, is added to the vacuum chamber, and a

10

15

20

25

30

WO 2005/034791 PCT/US2004/033534

capacitive RF plasma is ignited, causing the surfaces of the substrates to be bombarded with energetic ions (sputter-etched) to assist in the removal of residual hydrocarbons and surface oxides, and to activate the surfaces. After each of the substrate surfaces has been sputter-etched, a silicon-containing material layer is deposited by capacitive RF plasma deposition. This silicon-containing material layer may be either an adhesion layer for subsequent deposition of moissanite (silicon carbide) crystals, or may be "Si-doped". If this silicon-containing layer is an adhesion layer, the next step in the process is deposition of a top layer by capacitive RF plasma deposition. Once the chosen thickness of the moissanite (or other crystalline material) coating layer has been achieved, the deposition process is terminated by extinguishing the plasma. Finally, the vacuum chamber pressure is increased to atmospheric pressure, and the coated substrates are removed from the vacuum chamber.

In another preferred embodiment, the abrading portion is formed by electroplating the abrasive material onto the cutting segment, as is well known in the art.

Drill bit configurations for use in dentistry are well-known in the art, and will not be described in detail.

In one preferred embodiment of the present invention, the impregnated segment includes a continuous phase material impregnated with silicon carbide. Preferably, the continuous phase material includes a hard, erosion- and wear-resistant material, such as metal carbide, a refractory metal alloy, a ceramic, copper, a copper-based alloy, nickel, a nickel-based alloy, cobalt, a cobalt-based alloy, iron, an iron-based alloy, silver, or a silver-based alloy. The impregnated segment may include more than one type of abrasive material in addition to silicon carbide, as well as one or more sizes of abrasive material particles. The abrasive material may be coated with a single or multiple layers of metal coatings, as known in the art and disclosed in U.S. Pat. Nos. 4,943,488 and 5,049,164, the disclosures of each of which are hereby incorporated by reference in their entirety.

The support member of the inventive cutting element is preferably fabricated from a tough and ductile material, such as iron, an iron-based alloy, nickel, a nickel-based alloy, copper, a copper-based alloy, titanium, a titanium-based alloy, zirconium, a zirconium-based alloy, silver, or a silver-based alloy, and other tough and ductile materials that will withstand elevated temperatures, such as are experienced during sintering, brazing and bit furnacing. One preferred embodiment of the support member includes a segment-retaining portion and a drill bit attachment portion. In one preferred embodiment, the segment-

15

20

25

30

WO 2005/034791 PCT/US2004/033534

retaining portion of the support member may be secured to the impregnated segment. In another preferred embodiment, the segment-retaining portion of the support member may be continuous with the impregnated segment. The attachment portion of the support member is preferably insertable into a socket of a bit body and may be secured therein by brazing to the bit body, mechanical affixation, or other known processes. Alternatively, the support member may be secured to the bit body by integral infiltration therewith during fabrication thereof.

Another preferred embodiment of the present invention comprises a method for preparing a moissanite (silicon carbide) impregnated cutting element. A preferred method of producing crystal-impregnated cutting elements, which is disclosed in detail in 6,286,498, is herein incorporated by reference. The impregnated cutting element is prepared by assembling layers of metal matrix material that contain interspersed moissanite. Each layer is formed by distributing the moissanite into a layer of bonding metal matrix. Each layer, which is assembled to form a superabrasive impregnated cutting element, can be of the same distribution pattern and concentration, or the distribution pattern and/or concentration may vary from layer to layer. These layers are then assembled to form the desired three-dimensional body. Subsequently the moissanite tool is consolidated by sintering or infiltration.

Another preferred embodiment of the present invention includes cutting materials comprising moissanite (silicon carbide). Cutting devices in accordance with one preferred embodiment of the present invention may include without limitation saw blades and glass cutters, and may advantageously be used in the field of semiconductor manufacturing in order to, for example, form silicon chips of different sizes and configurations.

Another preferred embodiment of the present invention includes abrasive materials comprising moissanite (silicon carbide). Abrasive materials, in accordance with one preferred embodiment of the present invention, may include without limitation sandpaper and files.

Although the foregoing description contains many specifics, these should not be construed as limiting the scope of the present invention, but merely as providing illustrations of some of the presently preferred embodiments. Similarly, other embodiments of the invention may be devised which do not depart from the spirit or scope of the present

PCT/US2004/033534

invention. All additions, deletions and modifications to the invention as disclosed herein which fall within the meaning and scope of the claims are to be embraced thereby.



10

20

25

PCT/US2004/033534

WHAT IS CLAIMED IS:

- 1. A drill bit, comprising a support member and a cutting element, wherein said cutting element comprises moissanite.
- 2. The drill bit of Claim 1, wherein the cutting element is impregnated with the 5 moissanite.
 - 3. The drill bit of Claim 1, wherein the cutting element is surface-coated with the moissanite.
 - 4. The drill bit of Claim 1, wherein said cutting element further comprises at least one additional compound selected from the group consisting of diamond, cubic zirconium, carbonitride, amorphous carbon, and hydrogenated amorphous carbon.
 - 5. The drill bit of Claim 1, wherein said support member and said cutting element are configured for use in a dental drill.
 - 6. The drill bit of Claim 1, wherein said moissanite has a particle size ranging from about 8 to about $150 \, \mu m^3$.
- 7. The drill bit of Claim 6, wherein said moissanite has a particle size ranging from about 25 to about 50 μm³.
 - A method for making a drill bit, comprising:
 coating a cutting element with moissanite by chemical vapor deposition.
 - 9. A method for making a drill bit, comprising: impregnating a cutting element with moissanite by assembling layers of metal matrix material that contain interspersed moissanite.
 - 10. The method of Claim 9, wherein each of the layers of metal matrix material has a different distribution pattern of moissanite.
 - 11. The method of Claim 9, further comprising: consolidating the layers of metal matrix material by sintering.
 - 12. A saw blade comprising moissanite.
 - 13. A glass cutter comprising moissanite.
 - 14. An abrasive material comprising moissanite.



INTERNATIONAL SEARCH REPORT

PCT/US2004/033534

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61C3/02 C23C16/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS	TO BE	RELEVANT
	 	

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/36711 A (KERR CORP) 25 May 2001 (2001-05-25) page 1, lines 2-4 page 7, line 15 - page 8, line 11 page 9, lines 10-23 page 11, lines 14-17 page 12, lines 2-12 page 13, lines 16-19	1,3-8, 12-14
X Y	US 6 390 819 B2 (RIITANO FRANCESCO) 21 May 2002 (2002-05-21) column 31, lines 34-61	1,2,4-7, 14 9-11
X	WO 02/067803 A (GORDON EUGENE I; MEDJET INC (US); TURDIU PARID (US)) 6 September 2002 (2002-09-06) page 4, lines 10,11	14

Further documents are listed in the continuation of box C.	X Patent family members are listed in annex.
Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filling date 'L' document which may throw doubts on priority claim(s) or which is cried to establish the publication date of another cladion or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filling date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle of theory underlying the invention. *X* document of particular relevance; the ctairned invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone. *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
Date of the actual completion of the international search 10 February 2005	Date of mailing of the international search report 18/02/2005
Name and malling address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Filjswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Chabus, H





INTERNATIONAL SEARCH REPORT

PCT/US2004/033534

		PC1/032004/033534
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Calegory *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 286 498 B1 (SUNG CHIEN-MIN) 11 September 2001 (2001-09-11) cited in the application column 4, line 7 - column 5, line 39	9-11



Form PCT/ISA/210 (continuation of second sheet) (January 2004)

page 2 or 4

INTERNATIONAL SEARCH REPORT

information on patent family members

PCT/US2004/033534

				1		•	
Patent document cited in search report		Publication date		Patent family member(s)		Publication date	
WO 0136711	Α	25-05-2001	AU WO	7729900 0136711	Α Δ1	30-05-2001 25-05-2001	
US 6390819	B2	23-08-2001	IT	RM950377		06-12-1996	
			US	6379155	B1	30-04-2002	
			US	6217335		17-04-2001	
			US	6059572		09-05-2000	
			US	6045362		04-04-2000	
			US	5775904		07-07-1998	
			US	2001016309		23-08-2001	
			US	2002037492		28-03-2002	
			US	2001041324		15-11-2001	
			CH	691163		15-05-2001	
			DE	19622401		12-12-1996	
			FR	2735012		13-12-1996	
			US	6042375		28-03-2000	
			US	2002090594		11-07-2002	
			บร	5642998		01-07-1997	
			ΑU	4035300		28-12-2000	
			BR	0011104		19-03-2002	-
			CA	2375675		14-12-2000	
			EP	1180984		27-02-2002	
			JP	2003501136	Ţ	14-01-2003	
			MX	PA01012513		30-07-2002	
			WO	0074589		14-12-2000	
		·	US 	6012921	A 	11-01-2000	
WO 02067803	A	06-09-2002	WO	02067803	A1	06-09-2002	
US 6286498	B1	11-09-2001	US	6039641		21-03-2000	
			US	2003084894		08-05-2003	
			US	2004112359		17-06-2004	
			US	2004194689		07~10~2004	
			US	2002077054	-	20-06-2002	
			AU	6586498		30-10-1998	
			CN	1252021	T	03-05-2000	
			EP	1015180		05-07-2000	
			JP	2000512219		19-09-2000	
			TW	394723		21-06-2000	
			MO	9845092		15-10-1998	
			US	6159286		12-12-2000	
			AU	6587698		30-10-1998	
			CN	1120766		10-09-2003	
			EP	1015182	_	05-07-2000	
			JP	2000512220	Ţ	19-09-2000	
			TW	414748		11-12-2000	
			WO US	9845091 6193770	A2	11-12-2000 15-10-1998 27-02-2001	1



Form PCT/ISA/210 (patent family annex) (January 2004)